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## (54) PHOSPHATE CATALYSTS USED IN ADIPONITRILE MANUFACTURE

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED Imperial Chemical House, Millbank, London SW1P 3JF a British Company do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 THIS INVENTION relates to the use of supported phosphate catalysts in the manufacture of adiponitrile.

Our invention provides a process for the manufacture of adiponitrile which comprises heating adipic acid with ammonia in the vapour phase in the presence of a phosphate catalyst supported on an aluminium silicate clay mineral. By an aluminium silicate mineral we mean a complex silicate containing aluminium in the lattice and possibly one or more other metals such as sodium, potassium, calcium or magnesium. Such minerals are to be distinguished from silica and hydrated silicas which have already been extensively used as catalyst supports.

Particularly important aluminium silicate clay minerals for use in preparing the catalysts used in the process of our invention are montmorillonite, bentonite (which contains montmorillonite), attapulgite (palygorskite), saponite and kaolinite. Of these, those clay minerals having fine needle-shaped particles are particularly important, notably attapulgite.

By a phosphate catalyst we mean phosphoric acid itself or a phosphate salt, for example ammonium, lithium, sodium or potassium dihydrogen phosphate, diammonium, disodium, dipotassium or dilithium hydrogen phosphate, and the corresponding magnesium and calcium phosphates.

The supported catalyst compositions used in our invention may be prepared by

coating the aluminium silicate mineral with phosphoric acid or the phosphate. The amount of phosphoric acid or phosphate used normally lies within the range of from 1% to 25% by weight of the aluminium silicate mineral. Coating may be effected, for example, by slurring the aluminium silicate mineral with an aqueous solution of phosphoric acid or a phosphate and then removing the water by evaporation, for example in a vacuum evaporator.

Before use the coated aluminium silicate mineral is preferably conditioned by heating, particularly by heating at temperatures within the range 250°C to 600°C for from 1 to 10 hours.

In the case of attapulgite washing of the mineral with acid to remove impurities prior to coating is desirable. For the purpose of converting adipic acid to adiponitrile the catalyst may be in a fixed bed or in a fluidised bed. The temperature of the reaction normally falls within the range 250°C to 500°C and the ammonia to adipic acid ratio within the molar range 4:1 to 20:1. The feed rate of adipic acid typically falls within the range 350 to 850 parts by weight/hour for each 1,000 parts of catalyst.

The invention is illustrated but not limited by the following Examples in which the parts and percentages are by weight.

### PREPARATION OF SUPPORTED CATALYST

#### EXAMPLE 1

Attapulgite was coated with 5% of its weight of phosphoric acid as follows:—

950 parts of attapulgite were charged to a solution of 50 parts of phosphoric acid in 1,500 parts of water. The slurry was placed in a solvent evaporator and the water removed by heating under reduced pressure. The moist coated attapulgite was dried by

heating at 130° C for 16 hours and was finally calcined by heating at 350°C for 3 hours.

#### EXAMPLE 2

- 5 Attapulgit was washed with 15% by weight hydrochloric acid until essentially free from acid- and water-soluble impurities, and was then washed with water until free from acid and dried. The dried material was coated with 10% of its weight of phosphoric acid, dried at 130°C for 16 hours and conditioned by heating for 3 hours at 350°C.

#### EXAMPLE 3

- 15 Attapulgit was acid-washed and dried as described in Example 2 and was then coated with 5% of its weight of phosphoric acid, dried at 130°C and calcined for 3 hours at 350°C.

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#### USE OF SUPPORTED CATALYST

#### EXAMPLE 4

- 25 Vapourised adipic acid at a temperature of 350°C to 390°C at a rate of 300 parts/hr. was premixed with superheated ammonia at 360° to 400°C) in a molar ratio of 1:8 and passed through a packed bed of 550 parts of the catalyst of Example 1 held at a temperature of 360°C.

- 30 The yield of adiponitrile, calculated on the adipic acid used, was 37% together with 30% of useful under conversion products ( $\delta$ -cyanovaleic acid,  $\delta$ -cyanovaleamide) suitable for further conversion to adiponitrile. Measured impurities were 5.7% and adipic acid degradation 1.1%.

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#### EXAMPLE 5

- 45 Vapourised adipic acid at a temperature of 350 to 390°C at a rate of 430 parts/hr. was premixed with superheated ammonia (at 360 to 400°C) in a molar ratio of 1:9, and the mixture passed upwards through a fluidised bed of 395 parts of the catalyst of Example 1 at 380°C.

- 50 The yield of adiponitrile, calculated on the adipic acid used, was 55% together with 17% of useful under conversion products. Measured impurities were 18% and adipic acid degradation 2.2%.

#### EXAMPLE 6

- 55 Vapourised adipic acid at 350 to 390°C at a rate of 360 to 370 parts/hr. was premixed with superheated ammonia (at 360 to 400°C) in a molar ratio of 1:8 and passed through a packed bed of 600 parts of the catalyst of Example 2 at 360°C.

- 60 The yield of adiponitrile, calculated on the adiponitrile used, was 84.3% together

with 6.2% of useful under conversion products. Impurities were 2.5% and adipic acid degradation 1.1%.

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#### EXAMPLE 7

Vapourised adipic acid at 350 to 390°C at a rate of 140 parts/hr. was premixed with superheated ammonia (at 360 to 400°C) in a molar ratio of 1:9 and passed through a fluidised bed reactor containing 330 parts of the catalyst of Example 3 at 380°C.

The yield of adiponitrile, calculated on the adipic acid used was 73.7% together with 8% of useful under conversion products. Impurities were 7% and adipic acid degradation 3.9%.

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#### WHAT WE CLAIM IS:—

1. A process for the manufacture of adiponitrile which comprises heating adipic acid with ammonia in the vapour phase in absence of a phosphate catalyst supported on an aluminium silicate clay mineral as hereinbefore defined.

2. A process as claimed in Claim 1 in which the aluminium silicate clay mineral is montmorillonite, bentonite, attapulgit, saponite or kaolinite.

3. A process as claimed in Claim 1 in which the clay mineral has fine needle-shaped particles.

4. A process as claimed in Claim 3 in which the clay mineral is attapulgit.

5. A process as claimed in any of Claims 1 to 4 in which the catalyst used is manufactured by a process in which an aluminium silicate clay mineral is slurried with an aqueous solution of phosphoric acid or a phosphate and water is then removed by evaporation to give a coated aluminium silicate clay mineral.

6. A process as claimed in Claim 5 in which the coated aluminium silicate clay mineral is conditioned by heating at a temperature within the range 250°C to 600°C.

7. A process as claimed in either of Claims 5 or 6 in which the aluminium silicate clay mineral is attapulgit, and the attapulgit is washed with acid to remove impurities prior to coating.

8. A process for the manufacture of adiponitrile substantially as herein described and illustrated with reference to any one of the Examples.

9. Adiponitrile whenever manufactured by a process as claimed in any of the preceding claims.

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